Transformations of spirocyclodimers of 1,3-bis(ferrocenylmethylidene)-2-methylidenecycloalkanes in acid medium

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An intramolecular homoannular alkylation of one ferrocenyl substituent in spirocyclodimers of 1,3-bis(ferrocenylmethylidene)-2-methylidenecyclohexanes and -cycloheptanes on treatment with trifluoroacetic acid, leading to the formation of polyfused products containing a three-petal system of six-membered rings in the molecule center, was found. The structure of 11-ferrocenyl-6,14-bis(ferrocenylmethylidene)-2,3-ferroceno-1,2-tetracyclo[8.8.0.0^{5,10}.0^{13,18}]octadeca-2,13(18)-diene was established by X-ray diffraction analysis.

Key words: ferrocene, s-*cis*-1,3-bis(ferrocenylmethylidene)-2-methylidenecycloalkanes, ferrocenylpolycycloalkanes, alkylation, X-ray diffraction analysis.

Previously,[1—4] we reported the synthesis of exocyclic diferrocenyl-substituted conjugated trienes **1a**,**b** and investigation of their behavior in the cationic cycloaddition reaction. It was found that trienes **1a**,**b** undergo acid-catalyzed cyclodimerization, formally, according to the Diels—Alder reaction pattern to give spirocyclodimers **2** and **3**, both unsubstituted and substituted methylene groups being involved in the reaction as the dienophile[1—7] (Scheme 1).

Trienes **1a**,**b** also add salts of 1,5-diferrocenyl-3-methyl-1,4-dienyl cations **4a**,**b** at the exocyclic methylene group to give mixtures of cyclic dimers **3a**,**b** and linear 1,4-addition products **5a**,**b** (Scheme 2).

The structures of compounds **2a**,**b** and **3a**,**b** were established using ^{1}H and ^{13}C NMR data; however, their chemical properties have been barely studied.

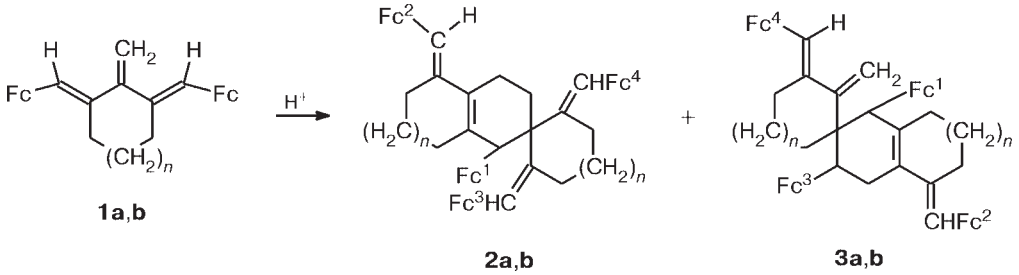
To continue the investigations of the spirocyclodimers, here we studied the transformations of compounds **2** and **3** in acid media.

Results and Discussion

We found that treatment of cyclodimers **2** and **3** with excess CF_3COOH furnishes products whose structure depends on the position of the ferrocenyl substituent Fc^1 in the initial dimer. Thus spiranes **2a**,**b** are converted into fused compounds **6a**,**b** (~60—65%), while spiranes **3a**,**b** give compounds **7a**,**b** (~40—45%).

The ^{1}H NMR spectra of compounds **6a** and **6b** exhibit four characteristic singlets due to protons of four unsubstituted C_5H_5 groups of the ferrocenyl substituents and two singlets for the olefinic protons of the two

Scheme 1



1a,**b** **2a**,**b** **3a**,**b**

Fc = $C_5H_5FeC_5H_4$; n = 1 (**a**), 2 (**b**)

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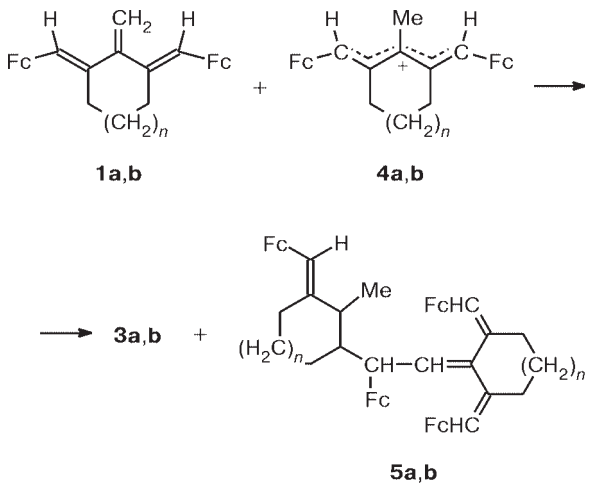
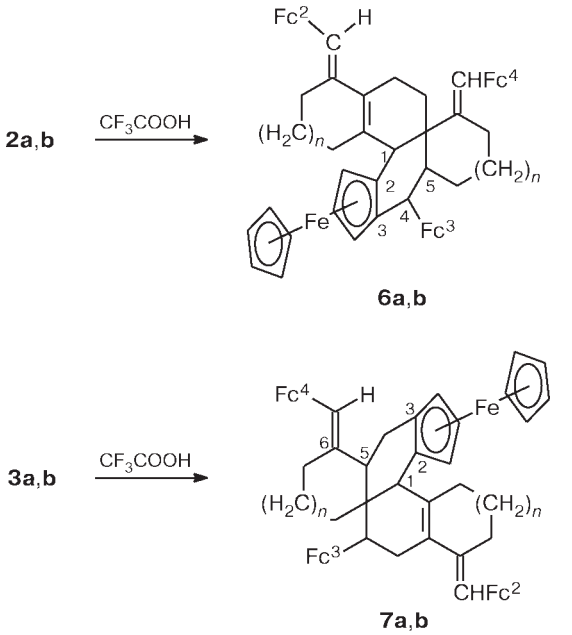
Scheme 2



n = 1 (**a**), 2 (**b**).

Scheme 3



n = 1 (**a**), 2 (**b**).

ferrocenylmethylidene fragments. The protons of the substituted cyclopentadienyl rings of ferrocene are recorded as a complex system of multiplets. The signals of the methine protons provide quite a lot of information; one of the signals is isolated and shows itself as a singlet, while the two others occupy vicinal positions with the spin-spin coupling constant $J \sim 6$ Hz, which is consistent with the structure of **6**. The presence of five signals for the quaternary carbon atoms of the ferrocenyl substituents in the ^{13}C NMR spectra of compounds **6a**,**b**, along with the signals due to four unsubstituted cyclopentadienyl rings of ferrocene, points unambiguously to the presence of one 1,2-disubstituted ferrocenyl fragment. The numbers of signals for the C, CH, and CH_2 groups and the values of chemical shifts in the ^{13}C NMR spectra are also fully consistent with structure **6**.

The structure of compounds **7a**,**b** was determined in a similar way. The ^1H NMR spectra also exhibit four singlets due to the four C_5H_5 groups of the ferrocenyl substituents and a singlet for one methine proton; however, as opposed to structure **6**, the two other methine protons show themselves as triplets not connected to each other.

In order to establish the spatial structure of the compounds, the single crystals of **7a** isolated by crystallization from chloroform were studied by X-ray diffraction analysis, according to which compound **7a** is actually 11-ferrocenyl-6,14-bis(ferrocenylmethylidene)ferroceno[1′,2′:2,3]tetracyclo[8.8.0.0^{5,10}.0^{13,18}]octadeca-2,13(18)-diene having a three-petal fused system of six-membered carbocycles around one nodal quaternary C(10) carbon atom in the center of the molecule (C(11) in Fig. 1). The main geometric parameters of compound **7a** are listed in Table 1. The average Fe^1—C distance is 2.025 Å, Fe^2—C is 2.035 Å, Fe^3—C is 2.051 Å, and Fe^4—C is 2.025 Å; the average C—C bond lengths in the cyclopentadienyl ringss are 1.390 (Fc^1), 1.406 (Fc^2), 1.414 (Fc^3), and 1.357 Å (Fc^4).

It is beyond doubt that compounds **6a**,**b** are formed upon intramolecular homoannular alkylation of the ferrocenyl substituent Fc^1 in the α-ferrocenyl carbocations **8a**,**b**, arising due to protonation of the ferrocenyl-

Table 1. Selected bond lengths (*d*) and angles (ω) in the structure of compound **7a**

Bond	*d*/Å	Angle	ω/deg
C(4)—C(21)	1.434(13)	C(10)—C(11)—C(6)	108.8(7)
C(4)—C(5)	1.502(11)	C(10)—C(11)—C(20)	106.0(6)
C(5)—C(6)	1.523(12)	C(20)—C(11)—C(6)	106.4(6)
C(6)—C(11)	1.575(11)	C(10)—C(11)—C(12)	113.8(6)
C(11)—C(20)	1.564(11)	C(6)—C(11)—C(12)	112.6(6)
C(20)—C(21)	1.498(13)	C(20)—C(11)—C(12)	108.7(6)
C(20)—C(19)	1.506(12)	C(13)—C(12)—C(11)	113.2(6)
C(19)—C(14)	1.326(12)	C(5)—C(6)—C(11)	113.3(7)
C(14)—C(13)	1.517(11)	C(21)—C(20)—C(11)	111.4(7)
C(13)—C(12)	1.562(11)	C(38)—C(12)—C(11)	115.1(7)
C(12)—C(11)	1.585(10)	C(19)—C(20)—C(11)	110.4(6)
C(11)—C(10)	1.558(11)	C(9)—C(10)—C(11)	116.9(7)
C(10)—C(9)	1.538(13)	C(5)—C(6)—C(11)	113.3(7)
C(8)—C(9)	1.526(13)	C(7)—C(6)—C(11)	112.1(7)
C(8)—C(7)	1.512(12)	C(21)—C(4)—C(5)	122.1(8)
C(6)—C(7)	1.526(12)	C(4)—C(21)—C(20)	123.1(8)

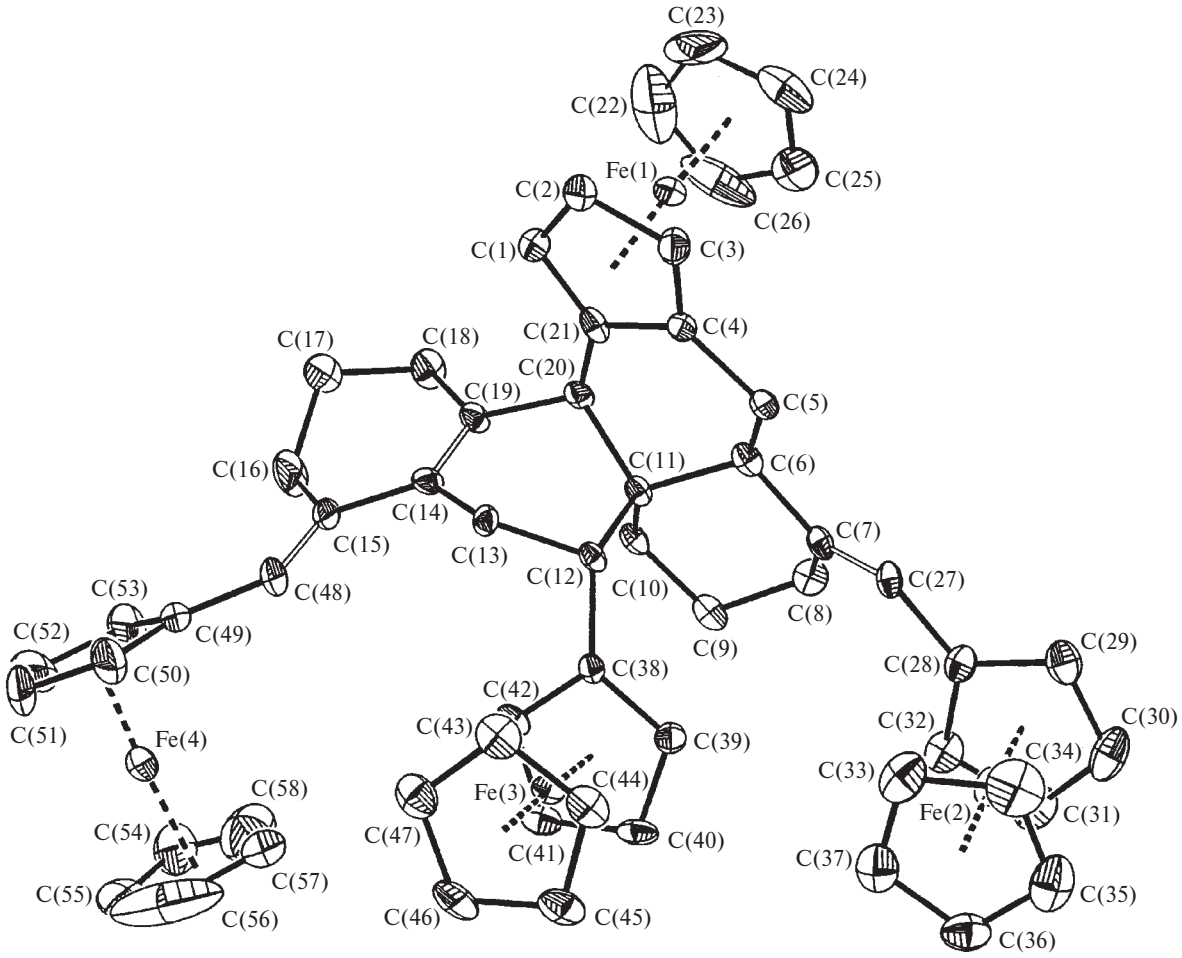
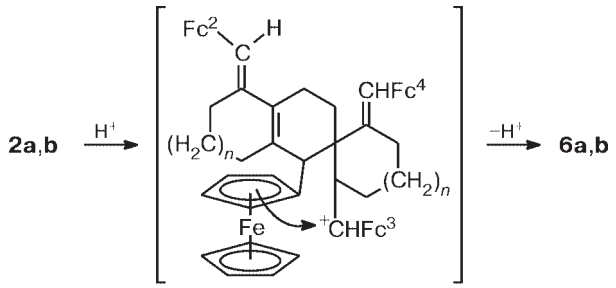


Fig. 1. Structure of molecule **7a**.

methylidene $Fc^3CH{=}C$ fragment in the initial cyclodimers **2** (Scheme 4).

Scheme 4



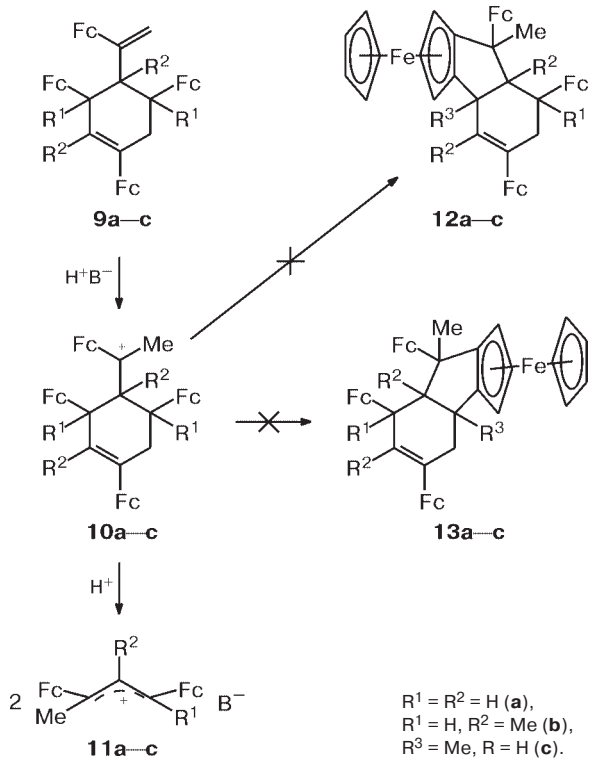
n = 1 (**a**), 2 (**b**)

Intramolecular homoannular alkylation of one of ferrocene substituents giving rise to carbocyclic polyfused compounds has been repeatedly observed previously[7–9] in the [4+2]-cycloaddition of 1,3-diferrocenyl, 1,3-diarylallyl, and phenylferrocenylcarbenium cations to ferrocenyl-1,3-butadienes. The H^+-catalyzed intramolecular alkylation of ferrocene in cyclodimers such as Diels—Alder adducts[10] is observed here for the first time. This outcome is, apparently, due to the absence of substantial steric hindrance of a conformational nature in cations **8a**,**b**, which is favorable for intramolecular alkylation giving compounds **6a**,**b**.

Unlike spirocyclodimers **2**, dimers **3** prepared by cationic cyclodimerization of trienes **1a**,**b** contain an olefinic CH_2 group and, in this respect, they resemble monocyclic ferrocenyl-sibstituted diterpenes **9a**—**c**, which are the products of the proton or cationic cyclodimerization of ferrocenyl-1,3-dienes.[11–13] It is known that on treatment with acids (CF_3COOH, HBF_4 etherate), ferrocenylditerpenes[12–14] are protonated at the $=CH_2$ double bond to give initially methylferrocenylcarbenium cations **10a**—**c**, which undergo fragmentation to give two molecules of **11a**—**c** (Scheme 5).

No products of intramolecular alkylation of the ferrocene substituents in positions 3 or 5 of the cyclohexene ring by the methylferrocenyl carbocationic center of type

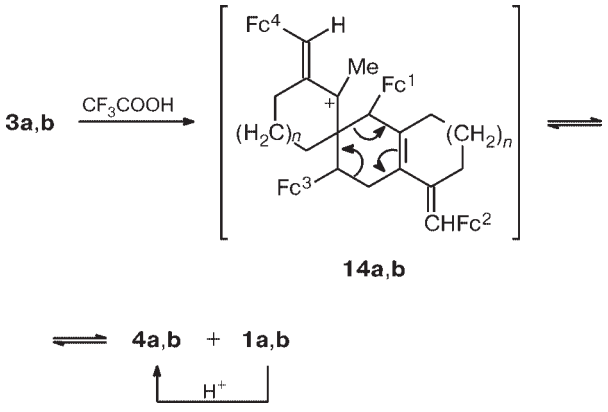
Scheme 5



12a—c or **13a—c** were detected, apparently, due to the fast fragmentation of the dimeric cations **10a—c**.

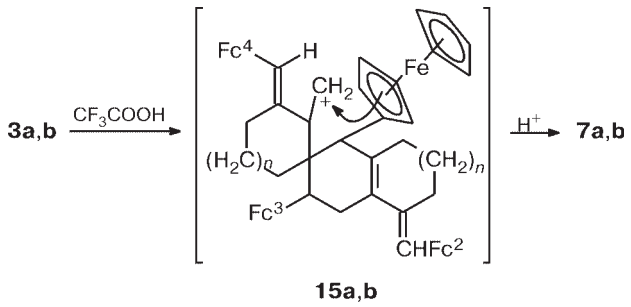
Initially, it was expected that spirocyclodimers **3** will also be protonated on treatment with acids and be fragmented in a similar way (Scheme 6).

Scheme 6



However, spirocyclodimers **3a**,**b** differ essentially from ferrocenylditerpenes **9a—c** as they do not undergo fragmentation on treatment with CF_3COOH; in our opinion, this indicates that fragmentation of the spirane carbenium cations **14a**,**b** to dienyl cations **4a**,**b** and trienes **1a**,**b** is difficult. This retardation of the fragmentation process may be related to the fact that the allylic **14a**,**b** and dienyl **4a**,**b** cations are approximately equally stable.[15,16] As a consequence, the unstable primary carbenium cations **15a**,**b** arising in the reaction mixture in minor amounts are capable of alkylating the spatially proximate ferrocene substituent Fc^1 to give compounds **7** (Scheme 7).

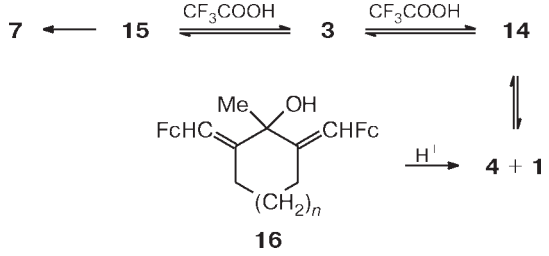
Scheme 7



The conformational factors are, apparently, favorable for the formation of alkylation products **7a**,**b** with closure of a new six-membered ring.

Evidently, fragmentation of spiranes **3a**,**b** could be attained if diferrocenyldienyl cations **4a**,**b** are removed from the equilibrium system as insoluble salts. Indeed, we found that fragmentation takes place when HBF_4 in ether is used as the protonating agent. The tetrafluoroborates of 1,5-diferrocenyl-3-methyl-1,4-dienyl cations **4**, insoluble in ether, are isolated in virtually quantitative yields (Scheme 8).

Scheme 8



n = 1, 2.

The structure of salts **4a**,**b** was confirmed by elemental analysis and ^1H NMR spectra, which completely coincide with these data for the corresponding salts prepared previously[1—3] from bis(ferrocenylmethylidene)methylcycloalkanols **16a**,**b**.

Spirocyclodimers **2a**,**b** do not undergo fragmentation on treatment with HBF_4 etherate but form, instead, the

products of intramolecular alkylation **6a**,**b**, as in the reaction with CF_3COOH.

In these reactions, attention is attracted by high stereoselectivity in the formation of compounds **6** and **7**. The presence of several asymmetric centers and the chiral 1,2-annelated ferrocene fragment in the products might give rise to numerous diastereomers (even if the structures obviously unfavorable for steric reasons are neglected); however, this is not the case. Compounds **6a**,**b** and **7a**,**b** were isolated as single diastereomers. Some amounts of other isomers might also be formed but the low contents of these compounds preclude their reliable identification in the reaction products. The high stereoselectivity of cationic alkylation should, apparently, be attributed to the configurational stability of α-ferrocenyl carbocations[16] and to specific features of these reactions, whose stereochemistry has not yet been studied.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) in $CDCl_3$ with $SiMe_4$ as the internal standard. The ^1H NMR spectra of tetrafluoroborates **4a**,**b** were recorded in a solution of CD_2Cl_2. Column chromatography was carried out using Al_2O_3 (Brockman activity III) and plates with a fixed SiO_2 layer. All reactions were carried out in a stream of dry nitrogen.

The unit cell parameters and the intensities of reflections were measured on a Siemens P4/PC diffractometer at 293 K (Table 2).

The following commercial reagents (Aldrich) were used: ferrocenylcarbaldehyde, 99%; cyclohexanone, 99%; cycloheptanone, 99%; trifluoroacetic acid, 99%; anhydrous pyridine, 99.8%; phosphorus oxochloride, 99.99%; and methyllithium (a 1.4 *M* solution in diethyl ether); $HBF_4 \cdot Et_2O$, 50—52%, was an Alfa AESAR commercial preparation. Diethyl ether was dried with $CaCl_2$ and dehydrated by distillation from sodium diphenylketyl. CH_2Cl_2 was washed with concentrated H_2SO_4, water, 10% NaOH, and again water, dried over annealed K_2CO_3, and distilled over 4Å molecular sieves.

1,3-Bis(ferrocenylmethylidene)-2-methylidenecycloalkanes 1a,**b** were prepared by dehydration of carbinols **16a**,**b** by a previously reported procedure.[14]

Spirocyclodimers 2a,**b** were synthesized by thermal cyclodimerization of trienes **1a**,**b** (see Refs. 1—3).

Spirocyclodimers 3a,b. A solution of alcohols **16a**,**b** (3.0 mmol) in 200 mL of glacial CH_3COOH was refluxed with stirring for 2 h and diluted with 200 mL of water. The products were extracted with benzene (3×50 mL). The combined benzene extracts were washed several times with water and the solvent was evaporated *in vacuo*. The residue was chromatographed on a column with Al_2O_3 (elution with hexane—benzene, 3 : 1). Cyclodimers **2a**,**b** (~18—32%) were the first to be eluted, while cyclodimers **3a**,**b** were the last. This gave **spiro[3-ferrocenylmethylidene-2-methylidenecyclohexane-1,2′-(1,3-diferrocenyl-5-ferrocenylmethylidene-1,2,3,4,5,6,7,8-octahydronaphthalene)] (3a)**, yield 53%, m.p. 262—263 °C (*cf.* Ref. 1) and **spiro[3-ferrocenylmethylidene-2-methylidenecycloheptane-1,7′-(6,8-diferrocenyl-1-ferrocenylmethylidene-2,3,4,5,6,7,8,9-octahydro-1*H*-benzocycloheptane)] (3b)**, yield 48%, m.p. 254—256 °C (*cf.* Ref. 3).

Table 2. Crystal structure parameters of compound **7a** and X-ray experiment details

Parameter	Value
Molecular formula	$C_{58}H_{56}Fe_4$
Molecular weight/g mol^{-1}	976.43
T/K	293
Crystal system	Monoclinic
Space group	*Cc*
a/Å	7.1480(1)
b/Å	28.028(3)
c/Å	22.445(2)α
α/deg	90.0
β/deg	98.48
γ/deg	90.0
V/Å^3	4447.6(9)
Z	4
d_{calc}/g cm^{-3}	1.458
Absorption coefficient/mm^{-1}	1.319
F(000)	2032
Radiation, λ/Å	Mo-Kα, 0.71073
Monochromator	Graphite
θ/2θ scanning range/deg	1.50—25.00
The number of reflections	79.01
The number of independent reflections	7283
R_{int}	0.0669
The number of refinement variables	570
Quality	1.022 (full-matrix least-squares method over F^2)
Residual electron density (ρ_{min}/ρ_{max})/e·Å^{-3}	−0.467/0.446
Weighing scheme	$w^{-1} = \sigma^2(Fo^2) + (0.0735P)^2$, where $P = (Fo^2 + 2Fc^2)/3$

Treatment of spirocyclodimers 2a,b with CF_3COOH. A solution of compound **2a**,**b** (1 mmol) in 50 mL of dry benzene and 20 mL of anhydrous CF_3COOH was refluxed with stirring for 48 h. Then 50 mL of water was added, and the organic layer was separated, washed several times with water, with a 5% solution of $NaHCO_3$, and again with water. After drying over $CaCl_2$, the solvent was evaporated *in vacuo,* and the residue was chromatographed on SiO_2 (TLC) (hexane—benzene, 2 : 1) to give 0.31 g (63%) of compound **6a**, R_f = 0.54; or 0.34 g (66%) of compound **6b**, R_f = 0.58.

4-Ferrocenyl-9,14-bis(ferrocenylmethylidene)ferroceno[1′,2′:2,3]tetracyclo[8.8.0.0^{5,10}.0^{13,18}]octadeca-2,13(18)-diene (6a), orange powder, m.p. 259—261 °C. Found (%): C, 71.18; H, 5.96; Fe, 23.06. $C_{58}H_{56}Fe_4$. Calculated (%): C, 71.34; H, 5.78; Fe, 22.88. ^1H NMR, δ: 1.64 (m, 2 H, CH_2); 1.84—1.99 (m, 4 H, 2 CH_2); 2.10—2.31 (m, 4 H, 2 CH_2); 2.42 (m, 2 H, CH_2); 2.58—2.74 (m, 4 H, 2 CH_2); 3.34 (m, 1 H, CH, J = 6.2 Hz, 7.0 Hz); 4.01 (s, 1 H, CH); 4.14 (d, 1 H, CH, J = 6.2 Hz); 4.03 (s, 5 H, C_5H_5); 4.10 (s, 5 H, C_5H_5); 4.18 (s,

5 H, C_5H_5); 4.22 (s, 5 H, C_5H_5); 3.89 (m, 2 H, C_5H_4); 4.06 (m, 1 H, C_5H_4); 4.15 (m, 2 H, C_5H_4); 4.20 (m, 4 H, C_5H_4); 4.25 (m, 3 H, C_5H_4); 4.31 (m, 1 H, C_5H_4); 4.36 (m, 2 H, C_5H_4); 6.02 (s, 1 H, CH=); 6.24 (s, 1 H, CH=). ^{13}C NMR, δ: 20.58, 21.63, 22.84, 23.38, 25.04, 27.94, 29.93, 34.41 (8 CH_2); 43.18 (CH); 52.49 (C_{spiro}); 61.24, 66.31 (2 Fc—CH); 65.61, 65.98, 66.19, 66.87, 67.12, 68.52, 68.91, 69.09, 69.18, 70.21, 70.25, 70.63, 70.90, 71.81, 72.13 (3 C_5H_4, 1 C_5H_3); 68.12, 68.35, 69.00, 70.11 (4 C_5H_5); 82.71, 83.54, 84.61, 84.99, 88.75 (5 C_{ipso}Fc); 121.14, 123.28 (2 CH=); 126.19, 129.82, 134.17, 138.12 (4 C).

4-Ferrocenyl-10,15-bis-(ferrocenylmethylidene)ferroceno[1′,2′:2,3]tetracyclo[9.9.0.0^{5,11}.0^{14,20}]eicosa-2,14(20)-diene (6b), orange powder, m.p. 287—288 °C. Found (%): C, 71.56; H, 6.20; Fe, 22.09. $C_{60}H_{60}Fe_4$. Calculated (%): C, 71.74; H, 6.02; Fe, 22.24. ^{1}H NMR, δ: 1.15 (m, 4 H, 2 CH_2); 1.45 (m, 4 H, 2 CH_2); 1.68 (m, 2 H, 1 CH_2); 1.74 (m, 2 H, 1 CH_2); 1.86 (m, 2 H, 1 CH_2); 2.14 (m, 2 H, 1 CH_2); 2.36 (m, 2 H, 1 CH_2); 2.65 (m, 2 H, 1 CH_2); 3.08 (m, 1 H, CH, J = 5.8 Hz, 6.4 Hz); 3.98 (s, 1 H, CH); 4.14 (d, 1 H, CH, J = 5.8 Hz); 4.06 (s, 5 H, C_5H_5); 4.12 (s, 5 H, C_5H_5); 4.19 (s, 5 H, C_5H_5); 4.24 (s, 5 H, C_5H_5); 3.85 (m, 2 H, C_5H_4); 4.08 (m, 2 H, C_5H_4); 4.13 (m, 1 H, C_5H_4); 4.20 (m, 2 H, C_5H_4); 4.28 (m, 2 H, C_5H_4); 4.32 (m, 3 H, C_5H_4); 4.34 (m, 1 H, C_5H_4); 4.39 (m, 2 H, C_5H_4); 6.05 (s, 1 H, CH=); 6.29 (s, 1 H, CH=). ^{13}C NMR, δ: 20.05, 22.18, 24.48, 26.73, 28.95, 29.72, 29.80, 30.18, 31.42, 32.22 (10 CH_2); 41.63 (CH); 54.12 (C_{spiro}); 64.03, 66.53 (2 Fc-CH); 67.27, 67.41, 67.54, 68.14, 68.20, 68.51, 68.70, 68.98, 69.26, 69.53, 69.57, 70.03, 70.19, 70.38, 71.05 (3 C_5H_4, 1 C_5H_3); 68.85, 69.10, 69.21, 69.29 (4 C_5H_5); 81.52, 81.64, 81.99, 82.31, 88.16 (5 C_{ipso}Fc); 122.75, 123.08 (2 CH=); 127.20, 130.01, 133.37, 139.01 (4 C).

Treatment of spirocyclodimers 3a,b with CF_3COOH. Anhydrous CF_3COOH (10 mL) was added with stirring to a solution of compound **3a**,**b** (1 mmol) in 50 mL of anhydrous CH_2Cl_2. The mixture was stirred for 72 h at 20 °C, washed with water, a 5% solution of $NaHCO_3$, and again with water and dried over $CaCl_2$. The solvent was evaporated *in vacuo* and the residue was chromatographed on SiO_2 (TLC) (hexane—benzene, 2 : 1) to give 0.16 g (31%) of the initial dimer **3a**, R_f = 0.60, m.p. 262—263 °C and 0.22 g (42%) of compound **7a**, R_f = 0.43; 0.13 g (23%) of the initial **3b**, R_f = 0.62, m.p. 255—256 °C and 0.24 g (45%) of compound **7b**, R_f = 0.46.

11-Ferrocenyl-6,14-bis(ferrocenylmethylidene)ferroceno[1′,2′:2,3]tetracyclo[8.8.0.0^{5,10}.0^{13,18}]octadeca-2,13(18)-diene (7a), pale yellow crystals, m.p. 272—273 °C. Found (%): C, 71.45; H, 5.69; Fe, 23.01. $C_{58}H_{56}Fe_4$. Calculated (%): C, 71.34; H, 5.78; Fe, 22.88. ^{1}H NMR, δ: 1.49 (m, 2 H, CH_2); 1.74—1.88 (m, 4 H, 2 CH_2); 2.06 (m, 2 H, CH_2); 2.25 (m, 2 H, CH_2); 2.52 (m, 2 H, CH_2); 2.78 (d, 2 H, CH_2, J = 7.2 Hz); 2.89 (d, 2 H, CH_2, J = 6.7 Hz); 3.98 (t, 1 H, CH, J = 6.7 Hz); 4.05 (t, 1 H, CH, J = 7.2 Hz); 4.12 (s, 1 H, CH); 4.06 (s, 5 H, C_5H_5); 4.09 (s, 5 H, C_5H_5); 4.11 (s, 5 H, C_5H_5); 4.12 (s, 5 H, C_5H_5); 3.95 (m, 1 H, C_5H_4); 4.0 (m, 1 H, C_5H_4); 4.13 (m, 4 H, C_5H_4); 4.15 (m, 4 H, C_5H_4); 4.18 (m, 2 H, C_5H_4); 4.21 (m, 2 H, C_5H_4); 4.33 (m, 1 H, C_5H_4); 5.45 (s, 1 H, CH=); 6.18 (s, 1 H, CH=). ^{13}C NMR, δ: 20.96, 22.63, 23.25, 28.12, 30.32, 31.57, 32.36, 41.51 (8CH_2); 45.13 (CH); 55.36 (C_{spiro}); 64.78, 65.06 (2 Fc—CH); 65.64, 66.96, 67.05, 67.51, 67.85, 68.12, 68.33, 68.82, 68.91, 69.02, 69.28, 69.56, 69.69, 70.18, 72.38 (3 C_5H_4, 1 C_5H_3); 68.28, 68.77, 69.02, 69.94 (4C_5H_5); 83.65, 84.40, 85.37, 87.57, 92.78 (5 C_{ipso}Fc); 118.14, 118.18 (2 CH=); 127.95, 135.30, 135.67, 139.31 (4 C).

12-Ferrocenyl-6,15-bis-(ferrocenylmethylidene)ferroceno[1′,2′,2,3]tetracyclo[9.9.0.0^{5,11}.0^{14,20}]eicosa-2,14(20)-diene (7b), yellow powder, m.p. 280—281 °C. Found (%): C, 71.89; H, 5.86; Fe, 22.35. $C_{60}H_{60}Fe_4$. Calculated (%): C, 71.74; H, 6.02; Fe, 22.24. ^{1}H NMR, δ: 1.05 (m, 4 H, 2 CH_2); 1.25 (m, 2 H, CH_2); 1.78 (m, 2 H, CH_2); 1.92 (m, 2 H, CH_2); 2.0 (m, 4 H, 2 CH_2); 2.29 (m, 2 H, CH_2); 2.65 (d, 2 H, CH_2, J = 6.6 Hz); 2.78 (d, 2 H, CH_2, J = 7.0 Hz); 4.01 (t, 1 H, CH, J = 7.0 Hz); 4.08 (t, 1 H, CH, J = 6.6 Hz); 4.11 (s, 1 H, CH); 4.13 (s, 5 H, C_5H_5); 4.15 (s, 5 H, C_5H_5); 4.17 (s, 5 H, C_5H_5); 4.21 (s, 5 H, C_5H_5); 4.04 (m, 2 H, C_5H_4); 4.06 (m, 1 H, C_5H_4); 4.18 (m, 2 H, C_5H_4); 4.23 (m, 2 H, C_5H_4); 4.27 (m, 2 H, C_5H_4); 4.29 (m, 2 H, C_5H_4); 4.36 (m, 1 H, C_5H_4); 4.42 (m, 2 H, C_5H_4), 4.47 (m, 1 H, C_5H_4); 5.91 (s, 1 H, CH=); 6.25 (s, 1 H, CH=). ^{13}C NMR, δ: 19.95, 20.89, 25.91, 26.38, 26.77, 29.32, 29.66, 30.83, 34.29, 36.80 (10 CH_2); 41.72 (CH); 55.31 (C_{spiro}); 64.24, 65.89 (2 Fc—CH); 66.53, 67.09, 67.48, 67.59, 67.75, 68.34, 68.61, 68.67, 68.86, 69.13, 69.42, 69.93, 70.02, 70.53, 70.64 (3 C_5H_4, 1 C_5H_3); 68.53, 68.91, 69.06, 69.32 (4 C_5H_5); 82.78, 83.26, 85.37, 92.41, 92.76 (5 C_{ipso}Fc); 121.12, 121.98 (2 CH=); 127.32, 132.31, 137.47, 138.29 (4 C).

Fragmentation of spirocyclodimers 3a,b. To a solution of compounds **3a**,**b** (1 mmol) in 100 mL of anhydrous ether, HBF_4 etherate (3 mL) was added dropwise with stirring. The mixture was stirred for 1 h at 20 °C. The nearly black precipitate was filtered off, washed on a filter with several portions of anhydrous ether, and dried in a vacuum desiccator to give 0.51 g (88%) of tetrafluoroborate **4a** and 0.54 g (90%) of tetrafluoroborate **4b**. **Compound 4a**, dec. at ~230 °C.[1] **Compound 4b**, dec. at ~300 °C (*cf.* Ref. 3).

Treatment of spirocyclodimers 2a,b with HBF_4 etherate. To a solution of compounds **2a**,**b** (1 mmol) in 50 mL of anhydrous CH_2Cl_2, HBF_4 etherate (2 mL) was added dropwise. The mixture was stirred for 5 h at 20 °C, and 50 mL of water was added. The organic layer was separated from the aqueous one, washed several times with water, a 5% solution of $NaHCO_3$, and again with water, and dried with $CaCl_2$, the solvent was evaporated *in vacuo*, and the residue was chromarographed on SiO_2 (TLC) (hexane—benzene, 2 : 1) to give 0.29 g (60%) of compound **6a**, R_f = 0.54, m.p. 259—261 °C; 0.32 g (63%) of compound **6b**, R_f = 0.58, m.p. 287—288 °C.

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